(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 967 248 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
29.12.1999 Bulletin 1999/52

(51) Int. Cl.^{6}: C08L 27/12
// (C08L27/12, 27:12, 27:12)

(21) Application number: 99111563.5

(22) Date of filing: 15.06.1999

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 23.06.1998 IT MI981429

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(54) Curable fluoroelastomeres by peroxidic way

(57) Curable fluoroelastomers essentially formed by the following fluoroelastomer mixtures:

a) from 20 to 70% by weight of a fluoroelastomer having the Mooney viscosity value, ML (1+10) at 121 °C higher than 60 points and containing from 0.01 to 3% by weight of iodine;
b) from 0 to 70% by weight of a fluoroelastomer having the Mooney viscosity value, ML (1+10) at 121 °C, in the range 20-60 points and containing from 0.2 to 5% by weight of iodine;
c) from 5 to 60% by weight of a fluoroelastomer having the Mooney viscosity value, ML (1+10) at 121 °C, in the range 1-20 points and containing an iodine percentage by weight higher than 0.3; said Mooney viscosity ML (1+10) at 121°C being determined according to the ASTM D 1646 method;

where said fluoroelastomers comprise monomeric units deriving from a bis-olefin.

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Description

[0001] The present invention relates to new fluoroelastomers cured by peroxidic way having improved mechanical and elastic properties.

[0002] Various fluoroelastomer types are known, widely used in those fields wherein outstanding elastic properties combined with high thermochemical stability are required, in the art. For a review of such products see for instance "Ullmann's Encyclopedia of Industrial Chemistry", vol. A-11, pag.417-429 (1988, VCH Verlagsgesellschaft).

[0003] The fluoroelastomer curing can be carried out both io-nically and by peroxides. In the first case, to the fluoroelastomer suitable curing agents (for instance polyhydroxylated compounds) associated to accelerants (for instance tetra-alkylammonium, tetraalkylphosphonium, phosphoranamines salts) are added. In the peroxidic curing case, the polymer must contain curing sites capable to form radicals in the presence of peroxides. To this purpose cure-site monomers containing iodine and/or bromine can be introduced in the polymeric backbone as described for example in USP 4,035,565, USP 4,745,165 and EP 199,138. Alternatively chain transfer agents containing iodine and/or bromine, which produce iodinated and/or brominated end groups (see for example USP 4,243,770 and USP 5,173,553), can be used during the polymerization.

[0004] A drawback of the compounds for curing resides in a difficult processing. In particular it is well known that the fluoroelastomers cured by peroxidic way show, with respect to those cured by ionic way, worse elastic properties as shown by the high compression set values. Besides there is a remarkable mold fouling causing a decrease of productivity and an increase of wastes.

[0005] The Applicant has surprisingly and unexpectedly found that it is possible to obtain new fluoroelastomers having superior mechanical, and compression set properties and excellent mold release properties.

[0006] An object of the present invention consists in curable fluoroealstomers substantially consisting of mixtures of the following flurooelastomers:

a) from 20 to 70% by weight of a fluoroelastomer having a Mooney viscosity, ML (1+10) at 121 °C, measured according to ASTM D 1646 method, higher than 60 points and contaianing from 0.01 to 3% by weight of iodine;
b) from 0 to 70% by weight of a fluoroelastomer having a Mooney viscosity, ML (1+10) at 121 °C, measured according to ASTM D 1646 method, greater than 20 to 60 points and containing from 0.2 to 5% by weight of iodine;
c) from 5 to 60% by weight of a fluoroelastomer having a Mooney viscosity, ML (1+10) at 121 °C, measured according to ASTM D 1646 method, in the range 1-20 points and containing an iodine percentage by weight higher than 0.3;

said fluoroelastomers comprise monomeric units deriving from a bis-olefin having the general formula:

$$R_1R_2\,C = \underset{\displaystyle R_3}{\underset{|}{C}} - Z - \underset{\displaystyle R_4}{\underset{|}{C}} = CR_5R_6 \qquad \text{(I)}$$

wherein:

R_1, R_2, R_3, R_4, R_5, R_6, equal to or different from each other, are H or C_1-C_5 alkyls;

Z is a C_1-C_{18} alkylene or cycloalkylene radical, linear or branched, optionally containing oxygen atoms, preferably at least partially fluorinated, or a (per)fluoropolyoxyalkylene radical.

[0007] Preferred compositions are the following:

a) from 20 to 50% by weight of a fluoroelastomer having a Mooney viscosity, ML (1+10) at 121 °C, measured according to ASTM D 1646 method, hgiher than 70 points and containing from 0.05 to 2% by weight of iodine;
b) from 0 to 50% by weight of a fluoroelastomer having a Mooney viscosity, ML (1+10) at 121 °C, measured according to ASTM D 1646 method, in the range 30-50 points and containing from 0.2 to 3% by weight of iodine;
c) from 10 to 30% by weight of a fluoroelastomer having a Mooney viscosity, ML (1+10) at 121 °C, measured according to ASTM D 1646 method, in the range 5-15 points and containing an iodine percentage by weight higher than 0.5.

[0008] In formula (I) Z preferably is a C_4-C_{12} perfluoroalkylene radical, wherein R_1, R_2, R_3, R_4, R_5, R_6 preferably are hydrogen.

[0009] When Z is a (per)fluoropolyoxyalkylene radical, it preferably has the formula:

$$-(Q)_p-CF_2O-(CF_2CF_2O)_m(CF_2O)_n-CF_2-(Q)_p- \qquad (II)$$

wherein: Q is a C_1-C_{10} alkylene or oxyalkylene radical; p is 0 or 1; m and n are integers such that the m/n ratio is between 0.2 and 5 and the molecular weight of said (per)fluoropolyoxyalkylene radical is in the range 500-10,000, preferably 1,000-4,000. Preferably, Q is selected from: $-CH_2OCH_2-$; $-CH_2O(CH_2CH_2O)_sCH_2-$, s=1-3.

[0010] The bis-olefins of formula (I) wherein Z is an alkylene or cycloakylene radical can be prepared, for example, according to I.L. Knunyants et al in Izv. Akad. Nauk. SSSR, Ser. Khim., 1964(2), 384-6, while the bis-oelfins containing (per)fluoropolyoxyalkylene sequences are described in USP 3,810,874.

[0011] The units deriving from such bis-olefins in the backbone are generally in the range 0.01-1.0 moles, preferably 0.03-0.5 moles, still more preferably 0.05-0.2% moles per 100 moles of the other monomer in the backbone.

[0012] The base structure of the fluoroelastomer can be in particular selected from:

(1) VDF-based copolymers, wherein VDF is copolymerized with at least a comonomer selected from: C_2-C_8 perfluoroolefins, such as tetrafluoroethylene (TFE), hexafluoropropene (HFP); chloro- and/or bromo- and/or iodo- C_2-C_8 fluoroolefins, such as chlorotrifluoroethylene (CTFE) and bromotrifluoroethylene; (per)fluoroalkylvinylethers (PAVE) CF_2=$CFOR_f$, wherein R_f is a C_1-C_6 perfluoroalkyl, for example trifluoromethyl, bromodifluoromethyl, pentafluoropropyl; perfluoro-oxyalkylvinylethers CF2=CFOX, wherein X is a C_1-C_{12} perfluoro-oxyalkyl having one or more ether groups, for example perfluoro-2-propoxy-propyl; non fluorinated (Ol) C_2-C_8 olefins, for example ethylene and propylene;

(2) TFE-based copolymers, wherein TFE is copolymerized with at least a comonomer selected from: (per)fluoroalkylvinylethers (PAVE) CF_2=$CFOR_f$, wherein R_f is as above defined; perfluoro-oxyalkylvinylethers CF_2=CFOX, wherein X is as above defined; C_2-C_8 fluoroolefins containing hydrogen and/or chlorine and/or bromine and/or iodine atoms; non fluorinated (Ol) C_2-C_8 olefins.

[0013] Within the above defined classes, preferred base monomer compositions are the following: (a) VDF 45-85%, HFP 15-45%, TFE 0-30%; (b) VDF 50-80%, PAVE 5-50%, TFE 0-20%; (c) VDF 20-30%, Ol 10-30%, HFP and/or PAVE 18-27%, TFE 10-30%; (d) TFE 50-80%, PAVE 20-50%; (e) TFE 45-65%, Ol 20-55%, VDF 0-30%; (f) TFE 32-60%, Ol 10-40%, PAVE 20-40%; (g) TFE 33-75%, PAVE 15-45%, VDF 5-30%.

[0014] The fluoroelastomer mixtures of the invention are obtainable by separately polymerizing the fluoroelastomers of points a), b) and c) and subsequently coagulating the latexes obtained in the above mentioned ratios. Alternatively the a), b) and c) fluoroelastomer mixture can be obtained in situ in a single polymerization by suitably dosing, as well known to the skilled in the art, the polymerization components during the polymerization reaction.

[0015] The preparation of the fluoroelastomers object of the present invention can be carried out by copolymerization of the monomers in aqueous emulsion according to well known methods, in the presence of radical initiators (for example alkaline or ammonium persulphates, perphosphates, perborates or percarbonates), optionally in combination with ferrous, cuprous or silver salts, or of other easily oxidizable metals. In the reaction medium also surfactants of various types are usually present, among which the fluorinated surfactants of formula:

$$R_f\text{-}X^- M^+$$

are particularly preferred, wherein R_f is a C_5-C_{16} (per)fluoroalkyl chain or a (per)fluoropolyoxyalkylene chain, X^- is $-COO^-$ or $-SO_3^-$, M^+ is selected from: H^+, NH_4^+, an alkaline metal ion. The most commonly used are: ammonium perfluorooctanoate, (per)fluoropolyoxyalkylenes ended with one or more carboxyl groups, etc.

[0016] The bis-olefin amount to be added to the reaction mixture depends on the amount desired in the final product. It has to be noted that, at the low amounts used according to the purposes of the present invention, practically all the bis-olefin present in the reaction medium enters into the chain.

[0017] When the copolymerization is completed, the fluoroelastomer is isolated by conventional methods, such as coagulation by addition of electrolytes or by cooling.

[0018] Alternatively, the polymerization reaction can be carried out in bulk, or in suspension in an organic liquid wherein a suitable radicalic initiator is present, according to well known techniques.

[0019] The polymerization reaction is generally carried out at temperatures in the range 25°-150°C, under pressure up to 10-MPa.

[0020] The preparation of the fluoroelastomers object of the present invention is preferably carried out in aqueous

emulsion in the presence of a perfluoropolyoxyalkylene emulsion, dispersion or microemulsion, according to USP 4,789,717 and USP 4,864,006.

[0021] The iodine containing fluoroelastomers of the present invention are curable by peroxidic way. Optionally the fluoroelastomers contain bromine atoms in the backbone as cure site or as terminal ends. The introduction of such iodine atoms, optionally bromine atoms, can be carried out by addition, in the reaction mixture, of brominated and/or iodinated cure-site comonomers, such as bromine and/or iodine olefins having from 2 to 10 carbon atoms (as described for example in USP 4,035,565 and USP 4,694,045), or iodine and/or bromine fluoroalkylvinylethers (as described in USP 4,745,165, USP 4,564,662 and EP-199,138). The bromine amount is substantially the same as the iodine amount or a bit larger.

[0022] In alternative, or also in association with the "cure-site" comonomers, it is possible to introduce terminal iodine atoms, optionally bromine atoms, by adding to the reaction mixture iodinated and/or brominated chain transfer agents, such as for example the compounds of formula $R_f(I)_x(Br)_y$, wherein R_f is a (per)fluoroalkyl or a (per)fluorochloroalkyl having from 1 to 8 carbon atoms, while x and y are integers in the range 0-2, with $1 \leq x+y \leq 2$ (see for example USP 4,243,770 and USP 4,943,622). It is also possible to use as chain transfer agents alkaline or earth-alkaline metal iodides and/or bromides, according to USP 5,173,553.

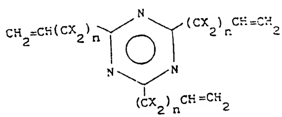
[0023] Optionally in association with the chain transfer agents containing iodine, optionally bromine, other chain transfer agents known in the art can be used, such as ethyl acetate, diethylmalonate, etc.

[0024] The peroxide curing is carried out, according to known techniques, by adding a suitable peroxide capable to generate radicals by heating.

[0025] Among the most commonly used, we can cite: dialkyl-peroxides, such as for example di-terbutyl-peroxide and 2,5-dimethyl-2,5-di(terbutylperoxy)hexane; dicumyl peroxide; dibenzoyl peroxide; diterbutyl perbenzoate; di[1,3-dimethyl-3-(terbutylperoxy)butyl]carbonate. Other peroxide systems are described, for example, in patent applications EP 136,596 and EP 410,351.

[0026] To the curing mixture other products are then added, such as:

(a) curing coagents, in amounts generally in the range 0.5-10%, preferably 1-7%, by weight with respect to the polymer; among them commonly used are: triallyl-cyanurate; triallyl-isocyanurate (TAIC); tris(diallylamine)-s-triazine; triallylphosphite; N,N-diallyl-acrylamide; N,N-,N',N'-tetraallyl-malonamide; trivinyl-isocyanurate; 2,4,6-trivinyl-methyltrisiloxane; N,N'bisallylbicyclooct-7-ene-disuccinimide (BOSA); bis olefin of formula (I), triazines having general formula



wherein X can independently be hydrogen, chlorine, fluorine C1-C3 alkyl or perfluoroalkyl; n is an integer in the range 2-20, preferably 4-12, more preferably 4-8. TAIC is particularly preferred.

(b) a metal compound, in amounts in the range 1-15% by weight, preferably 2-10%, with respect to the polymer, selected from oxides or hydroxides of divalent metals, such as for instance, Mg, Zn, Ca or Pb, optionally associated with a weak acid salt, such as for example, Ba, Na, K, Pb, Ca stearates, benzoates, carbonates, oxalates or phosphites;

(c) other conventional additives, such as thickeners, pigments, antioxidants, stabilizers and the like. It is also possible to use mixed curing systems, both ionic and peroxidic, as described in EP 136,596.

[0027] The Applicant has also found that the fluoroelastomers of the invention show a very good processability intended as higher productivity and reduction of wastes.

[0028] With the fluoroelastomers of the present invention it is possible to produce manufactured articles such as O-ring, shaft seal, gasket, etc., preferably O-ring having improved compression set.

[0029] The present invention will now be better illustrated by the following examples, which have a merely indicative, but not limitative purpose of the scope of the invention.

EXAMPLES

CHARACTERIZATION

Mooney viscosity ML(1+10') determined at 121°C (ASTM D1646)

[0030] On the obtained composition the curing curve by Oscillating Disk Rheometer (ODR) by Monsanto (Model 100 S) has been determined, according to the ASTM D2084-81 method, by operating at 177°C with a 3° oscillation amplitude.

[0031] The (ODR) data are reportd in the Tables: ML (minimum torque); MH (maximum torque); t_{s2} (time required for a torque increase of 2 lb.in over ML); t_{s50} (time required for a torque increase of 50 lb.in over ML); t'_{90} (time required for a torque increase of 50% and 90%, respectively).

[0032] On the cured product

- the compression set on O-ring at 200°C forr 70 h after postcuring at 200°C for 8 h (ASTM D395);
- the post-curing mechanical properties at 200°C for 8 h (ASTM D412-83) were determined and reported in the Tables.

EXAMPLE 1

EXAMPLE 1A

Average Mooney Polymer Synthesis

[0033] In a 22 l autoclave, equipped with stirrer working at 460 rpm, were introduced 14.5 l of demineralized water and 149.36 ml of a perfluoropolyoxyalkylene microemulsion previously obtained by mixing:

- 32.34 ml of an acid ended perfluoropolyoxyalkylene having the formula:

$$CF_3O(CF_2\text{-}CF(CF_3)O)_n(CF_2O)_mCF_2COOH$$

wherein n/m = 10 , having average molecular weight of 600;

- 32.34 ml of a 30% by volume NH_4OH aqueous solution;
- 64.68 ml of demineralized water;
- 20 ml of Galden® D02 of formula:

$$CF_3O(CF_2\text{-}CF(CF_3)O)_n(CF_2O)_mCF_3$$

wherein n/m = 20 , having average molecular weight of 450.

[0034] The autoclave was then heated to 85°C and maintained at such temperature for all the reaction duration. The following monomers mixture was then fed:

vinylidene fluoride (VDF)	60% by moles
perfluoromethylvinylether (MVE)	34% by moles
tetrafluoroethylene (TFE)	6% by moles

[0035] so as to bring the pressure to 30 bar.

[0036] In the autoclave were then introduced:

- 0.58 g of ammonium persulphate (APS) as initiator;
- 56.3 g of 1,6-diiodoperfluorohexane ($C_6F_{12}I_2$) as chain transfer agent;
- 27.8 g of bis-olefin of formula $CH_2{=}CH\text{-}(CF_2)_6\text{-}CH{=}CH_2$, the addition was carried out in 20 parts, each part of 1.39

g, beginning from the polymerization starting and for every 5% increase in the monomer conversion.

[0037] The 30 bar pressure was maintained constant for all the duration of the polymerization by feeding a mixture consisting of:

VDF	75% by moles
MVE	17% by moles
TFE	8% by moles

[0038] After 135 minutes of reaction, the autoclave was cooled, the latex discharged. 455 g/l of water of product with polymer Mooney viscosity, ML(1+10) at 121°C (ASTM D 1646), equal to 44, were thus obtained. The iodine percentage in the polymer is equal to 0.3% by weight. The molar composition measured by fluorine NMR is the following:

VDF	78.5% by moles
MVE	17.5% by moles
TFE	4% by moles

EXAMPLE 1B

High Mooney Polymer Synthesis

[0039] By following the same procedure described for the polymerization 1A, a polymer of the same type was prepared wherein the iodinated 1,6-diiodoperfluorohexane transfer agent amount was of 39 g.

[0040] After 107 minutes of reaction, the autoclave was cooled, the latex discharged. 441,4 g/l of water of product with polymer Mooney viscosity, ML(1+10) at 121°C (ASTM D 1646), equal to 94, were thus obtained. The iodine percentage in the polymer is equal to 0.2% by weight. The molar composition measured by fluorine NMR is the following:

VDF	78.5% by moles
MVE	17.0% by moles
TFE	4.5% by moles

EXAMPLE 1C

Low Mooney Polymer Synthesis

[0041] By following the same procedure described for the polymerization 1A, a polymer of the same type was prepared wherein the iodinated 1,6-diiodoperfluorohexane transfer agent amount was of 161.9 g and 24.4 of bisolefin fed in 20 parts, each part of 1.22 g.

[0042] After 140 minutes of reaction, the autoclave was cooled, the latex discharged. 458 g/l of water of product with polymer Mooney viscosity, ML(1+10) at 121°C (ASTM D 1646), equal to 7, were thus obtained. The iodine percentage in the polymer is equal to 0.45 by weight. The molar composition measured by fluorine NMR is the following:

VDF	79% by moles

(continued)

MVE	17.0% by moles
TFE	4.0% by moles

[0043] The latexes obtained by 1A, 1B, 1C syntheses were cocoagulated in the ratio: 40% by weight of latex 1A, 40% by weight of latex 1B and 20% by weight of latex 1C.

[0044] The Mooney viscosity (1+10) at 121°C (ASTM D 1646) of the so obtained polymer was equal to 50.

[0045] The polymer was then cured by peroxidic way: the blend composition and the characteristics of the cured product are reported in Table 1.

EXAMPLE 2 (comparative)

[0046] The synthesis 1A of Example 1 was repeated.

[0047] After 98 minutes of reaction, the autoclave was cooled, the latex discharged, coagulated, washed and dried. 455 g/l of water of product with polymer Mooney viscosity, ML(1+10) at 121°C (ASTM D 1646), equal to 48, were thus obtained. The iodine percentage in the polymer is equal to 0.32 % by weight. The molar composition measured by fluorine NMR is the following:

VDF	78.5 % by moles
MVE	17.0 % by moles
TFE	4.5 % by moles

[0048] The characteristics of the product cured by peroxidic way are reported in Table 1.

TABLE 1

EXAMPLE	1	2(*)
Blend composition		
Polymer (g)	100	100
Luperco(R) 101 XL (phr)	2	2
Drimix(R) TAIC (phr)	4.5	4.5
ZnO (phr)	4	4
Akrochem blue 602C (phr)	0.3	0.3
BaSO4 (phr)	35	35
Tremin 283 600 Est (phr)	35	35
Blend characteristics		
*Mooney viscosity ML(1+10') 121°C (ASTM D1646)	52	48
*ODR 177°C arc 3, 12' (ASTM D2084-81)		
ML (pounds • inch)	15	15
MH (pounds • inch)	134	136
t_{s2} (sec)	54	54
t_{s50} (sec)	87	90
t'_{90} (sec)	150	132
Characteristics after post-curing in stove at 230°C for 4 hours		
*MECHANICAL PROPERTIES (ASTM D412-83)		
Modulus at 100% (MPa)	6.0	5.2
Stress at break (MPa)	12.0	8.0
Elongation at break (%)	330	249
Shore A Hardness (points)	76	72
*COMPRESSION SET at 200°C for 70 hrs (ASTM D395 Method B)		
O-ring 214 (%)	23	29

(*) comparative

EXAMPLE 3

EXAMPLE 3A

Low Mooney Polymer Synthesis

[0049] In a 10 l autoclave, equipped with stirrer working at 545 rpm were introduced, after evacuation, 6.5 l of demineralized water and 67.18 ml of a perfluoropolyoxyalkylene microemulsion previously obtained by mixing:

- 14.27 ml of an acid ended perfluoropolyoxyalkylene of formula:

$$CF_3O(CF_2\text{-}CF(CF_3)O)_n(CF_2O)_mCF_2COOH$$

  wherein $n/m = 10$, having average molecular weight of 600;
- 14.27 ml of a 30% by volume NH_4OH aqueous solution;
- 28.54 ml of demineralized water;

- 10.1 ml of Galden(R) D02 of formula:

$$CF_3O(CF_2\text{-}CF(CF_3)O)_n(CF_2O)_mCF_3$$

wherein n/m = 20 , having average molecular weight of 450.

[0050] The autoclave was then heated to 80°C and maintained at such temperature for all the duration of the reaction. The following mixture of monomers was then fed:

vinylidene fluoride (VDF)	28% by moles
hexafluoropropene (HFP)	57% by moles
tetrafluoroethylene (TFE)	15% by moles

[0051] so as to bring the pressure to 30 bar.
[0052] In the autoclave were then introduced:

- 0.325 g of ammonium persulphate (APS) as initiator agent;
- 43.86 g of 1,6-diiodoperfluorohexane ($C_6F_{12}I_2$) as chain transfer agent;
- 5.6 g of bis-olefin having the formula $CH_2{=}CH\text{-}(CF_2)_6\text{-}CH{=}CH_2$, the addition was carried out in 20 parts, each of 0.28 g, beginning from the polymerization starting and for every 5% increment in the monomer conversion.

[0053] The 30 bar pressure was maintained constant for all the polymerization duration by feeding a mixture consisting of:

VDF	50% by moles
HFP	25% by moles
TFE	25% by moles

[0054] After 120 minutes of reaction, the autoclave was cooled, the latex discharged. 461.5 g/l of water of product with polymer Mooney viscosity, ML(1+10) at 121°C (ASTM D 1646), equal to 4, were thus obtained. The iodine percentage in the polymer is equal to 0.5 by weight. The molar composition measured by fluorine NMR is the following:

VDF	53% by moles
MVE	23% by moles
TFE	24% by moles

EXAMPLE 3B

High Mooney Polymer Synthesis

[0055] By following the same procedure described for the polymerization 3A, a polymer of the same type was prepared wherein the amount of iodinated 1,6-diiodoperfluorohexane transfer agent was 17.55 g.
[0056] After 118 minutes of reaction, the autoclave was cooled, the latex discharged. 455 g/l of water of product with polymer Mooney viscosity, ML(1+10) at 121°C (ASTM D 1646), equal to 80, were thus obtained. The iodine percentage in the polymer is equal to 0.19% by weight. The molar composition measured by fluorine NMR is the following:

VDF	53.5% by moles
HFP	23.5% by moles
TFE	23 % by moles

EXAMPLE 3C

Low Mooney Polymer Synthesis

[0057] By following the same procedure described for the polymerization 3A, a polymer of the same type was prepared wherein the iodinated 1,6-diiodoperfluorohexane transfer agent amount was 29.82 g.

[0058] After 110 minutes of reaction, the autoclave was cooled, the latex discharged. 460 g/l of water of product with polymer Mooney viscosity, ML(1+10) at 121°C (ASTM D 1646), equal to 21, were thus obtained. The iodine percentage in the polymer is equal to 0.35% by weight. The molar composition measured by fluorine NMR is the following:

VDF	53.5% by moles
HFP	23 % by moles
TFE	23.5% by moles

[0059] The latexes obtained by the 3A, 3B, 3C syntheses were cocoagulated in the ratio: 9% by weight of latex 3A, 45% by weight of latex 3B and 46% by weight of latex 3C.

[0060] The Mooney viscosity (1+10) at 121°C (ASTM D 1646) of the so obtained polymer was equal to 36.

[0061] The polymer was then cured by peroxidic way: the blend composition and the characteristics of the cured product are reported in Table 2.

EXAMPLE 4 (comparative)

[0062] By following the same procedure described for the polymerization 3A, a polymer of the same type was prepared wherein the iodinated 1,6-diiodoperfluorohexane transfer agent amount was 24.57 g.

[0063] After 115 minutes of reaction, the autoclave was cooled, the latex discharged. 460 g/l of water of product with polymer Mooney viscosity, ML(1+10) at 121°C (ASTM D 1646), equal to 37, were thus obtained. The iodine percentage in the polymer is equal to 0.32% by weight. The molar composition measured by fluorine NMR is the following:

VDF	53.5% by moles
HFP	23 % by moles
TFE	23.5% by moles

[0064] The characteristics of the cured product by peroxidic way are reported in Table 2.

TABLE 2

EXAMPLE		3	4(*)
Blend composition			
Polymer (g)		100	100
Luperco(R) 101 XL (phr)		3	3
Drimix(R) TAIC (phr)		4	4
ZnO (phr)		5	5
Carbon black MT (phr)		30	30
Blend characteristics			
*Mooney viscosity ML(1+10') 121°C (ASTM D1646)		37	40
*ODR 177°C arc 3, 12' (ASTM D2084-81)			
ML (pounds • inch)		8	8
MH (pounds • inch)		139	136
t_{s2} (sec)		57	58
t_{s50} (sec)		93	94
t'_{90} (sec)		120	120
V_{max} (pounds • foot • inch/sec)		2.9	2.9
Gottfert rheovulcanometer			
P=100 bar T_{room}=120°C T_{mold}=160°C			
t preheating=60sec			
t injection=70sec mold: spiral			
max flow-rate	mm3/sec	65	75
volume	mm3	1700	1800
Characteristics after post-curing in stove at 230°C for 1 h			
*MECHANICAL PROPERTIES (ASTM D412-83)			
Modulus at 100% (MPa)		7.8	8.2
Stress at break (MPa)		24.4	24.0
Elongation at break (%)		227	210
Shore A hardness (points)		75	76

(*) comparative

Claims

1. Curable fluoroelastomrs essentially formed by the following fluoroelastomer mixtures:

   a) from 20 to 70% by weight of a fluoroelastomer having a Mooney viscosity, ML (1+10) at 121 °C, higher than 60 points and containing from 0.01 to 3% by weight of iodine;
   b) from 0 to 70% by weight of a fluoroelastomer having Mooney viscosity, ML (1+10) at 121 °C greater than 20 to 60 points and containing from 0.2 to 5% by weight of iodine;
   c) from 5 to 60% by weight of a fluoroelastomer having a Mooney viscosity, ML (1+10) at 121 °C, in the range 1-20 points and containing an iodine percentage by weight higher than 0.3, said Mooney viscosity ML (1+10) at 121°C being measured according to the ASTM D 1646 method;
   where said fluoroelastomers comprise monomeric units deriving from a bis-olefin having the general formula:

$$R_1R_2\ C = \underset{\substack{|\\ R_3}}{C} - Z - \underset{\substack{|\\ R_4}}{C} = CR_5R_6 \qquad (I)$$

wherein:

R_1, R_2, R_3, R_4, R_5, R_6, equal to or different from each other, are H or C_1-C_5 alkyls;
Z is a C_1-C_{18} alkylene or cycloalkylene radical, linear or baranched, optionally containing oxygen atoms, preferably at least partially fluorinated, or a (per)fluoropolyoxyalkylene radical.

2. Fluoroelastomers according to claim 1 wherein the compositions are the following:

a) from 20 to 50% by weight of a fluoroelastomer having a Mooney viscosity ML (1+10) at 121 °C higher than 70 points and containing from 0.05 to 2% by weight of iodine;
b) from 0 to 50% by weight of a fluoroelastomer having a Mooney viscosity ML (1+10) at 121 °C in the range 30-50 points and containing from 0.2 to 3% by weight of iodine;
c) from 10 to 30% by weight of a fluoroelastomer having a Mooney viscosity ML (1+10) at 121 °C in the range 5-15 points and containing an iodine percentage by weight higher than 0.5.

3. Fluoroelastomers according to claims 1 and 2, wherein in the formula (I) Z is a C_4-C_{12} perfluoroalkylene radical, while R_1, R_2, R_3, R_4, R_5, R_6 are preferably hydrogen.

4. Fluoroelastomers according to claims 1 and 2 wherein Z is a perfluoropolyoxyalkylene radical, having the formula:

$$-(Q)_p-CF_2O-(CF_2CF_2O)_m(CF_2O)_n-CF_2-(Q)_p- \qquad (II)$$

wherein: Q is a C_1-C_{10} alkylene or oxyalkylene radical; p is 0 or 1; m and n are integers such that the m/n ratio is between 0.2 and 5 and the molecular weight of said (per)fluoropolyoxyalkylene radical is in the range 500-10,000.

5. Fluoroelastomers according to claims 1-4 wherein the chain unit amount deriving from such bis-olefins is in the range 0.01-1.0 moles, preferably 0.03-0.5 moles per 100 moles of the other base monomeric units.

6. Fluoroelastomers according to claim 5 wherein the chain unit amount deriving from such bis-olefins is in the range 0.05-0.2% moles.

7. Fluoroelastomers according to claims 1-6 wherein the base fluoroelastomer structure is selected from:

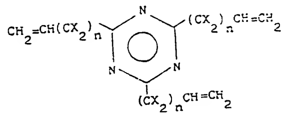
(1) VDF-based copolymers, wherein VDF is copolymerized with at least a comonomer selected from: C_2-C_8 perfluoroolefins, such as tetrafluoroethylene (TFE), hexafluoropropene (HFP); chloro- and/or bromo- and/or iodo- C_2-C_8 fluoroolefins, such as chlorotrifluoroethylene (CTFE) and bromotrifluoroethylene; (per)fluoroalkyl-vinylethers (PAVE) CF_2=$CFOR_f$, wherein R_f is a C_1-C_6 perfluoroalkyl, for example trifluoromethyl, bromodifluoromethyl, pentafluoropropyl; perfluoro-oxyalkylvinylethers CF2=CFOX, wherein X is a C_1-C_{12} perfluoro-oxyalkyl having one or more ether groups, for example perfluoro-2-propoxy-propyl; non fluorinated (Ol) C_2-C_8 oelfins, for example ethylene and propylene;
(2) TFE-based copolymers, wherein TFE is copolymerized with at least a comonomer selected from: (per)fluoroalkylvinylethers (PAVE) CF_2=$CFOR_f$, wherein R_f is as above defined; perfluoro-oxyalkylvinylethers CF_2=CFOX, wherein X is as above defined; C_2-C_8 fluoroolefins containing hydrogen and/or chlorine and/or bromine and/or iodine atoms; non fluorinated (Ol) C_2-C_8 olefins.

8. Fluoroelastomers according to claim 7 wherein the base monomer compositions are selected from:
(a) VDF 45-85%, HFP 15-45%, TFE 0-30%; (b) VDF 50-80%, PAVE 5-50%, TFE 0-20%; (c) VDF 20-30%, Ol 10-30%, HFP and/or PAVE 18-27%, TFE 10-30%; (d) TFE 50-80%, PAVE 20-50%; (e) TFE 45-65%, Ol 20-55%, VDF

0-30%; (f) TFE 32-60%, OI 10-40%, PAVE 20-40%; (g) TFE 33-75%, PAVE 15-45%, VDF 5-30%.

9. Fluoroelastomers according to claims 1-8 wherein the fluoroelastomers are cured by peroxidic way, wherein to the curing blend are added:

(a) curing coagents, in amount in the range 0.5-10%, preferably 1-7%, by weight with respect to the polymer; selected from: triallyl-cyanurate; triallylisocyanurate (TAIC); tris(diallylamine)-s-triazine; triallylphosphite; N,N-diallyl-acrylamide; N,N,N'-,N'-tetraallyl-malonamide; trivinyl-isocyanurate; 2,4,6-trivinyl-methyltrisiloxane;N,N'bisallylbicyclo-oct-7-ene-disuccinimide (BOSA); bis olefin of formula (I), triazines having general formula



wherein X can independently be hydrogen, chlorine, fluorine, C1-C3 alkyl or perfluoroalkyl; n is an integer in the range 2-20, preferably 4-12, more preferably 4-8.
(b) a metal compound, in amounts in the range 1-15%, preferably 2-10%, by weight with respect to the polymer, selected from oxides or hydroxides of divalent metals, prefeably Mg, Zn, Ca or Pb, optionally associated with a weak acid salt, such as Ba, Na, K, Pb, Ca stearates, benzoates, carbonates, oxalates or phosphites;
(c) other conventional additives, such as thickeners, pigments, antioxidants, stabilizers.

10. Use of the fluoroelastomers of claims 1-9, for preparing manufactured articles such as O-ring, shaft seals, gaskets.

11. Process for obtaining fluoroelastomers of claims 1-8 wherein said mixtures are obtained by separately polymerizing the fluoroelastomers of points a), b) and c) and subsequently co-coagulating the latexes obtained in the above mentioned ratios.

12. Process for obtaining fluoroelastomers of claims 1-8 wherein said fluoroelastomer mixtures a), b) and c) are obtained in situ in a single polymerization.

13. Process for obtaining fluoroelastomers according to claims 11 and 12 wherein the monomer polymerization is carried out in aqueous emulsion; in suspension.

14. Process for obtaining fluoroelastomers according to claim 13 wherein the monomer polymerization is carried out in aqueous emulsion in the presence of a perfluoropolyoxyalkylene emulsion, dispersion or microemulsion.

15. Process for obtaining fluoroelastomers according to claims 11-14 wherein the fluoroelastomer is isolated by conventional methods, preferably by coagulation.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 11 1563

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	5 October 1999	Friederich, P

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